Patent

Attorney's Docket No. <u>022701-859</u>

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of)	
)	
Giuseppe DI SILVESTRO et al)	Group Art Unit: 1714
)	
Application No.: 09/462,381)	Examiner: K. Wyrozebski-Lee
)	
Filed: March 27, 2000)	Confirmation No.: 5018
)	
For: THERMOPLASTIC)	
COPOLYAMIDE, COMPOSITION)	
BASED THEREON)	

DECLARATION PURSUANT TO 37 C.F.R. §1.132

Commissioner for Patents
Alexandria, VA 22313-1450

Sir:

I, Dr. Giuseppe Di Silvestro, declare and state as follows:

(1)   I have been employed by Universita' Degli Studi di Milano in Organic and Industrial Chemistry since November of 1972. My current title is Associate Professor of the Organic and Industrial Chemistry Department.

(2)   I was awarded a chemistry degree from State University of Milano.

(3)   My Curriculum Vitae, Research Experience and list of publications are attached hereto as Appendix I.

(4)   I am aware that the Examiner in the above-identified application has concluded that claims 17-21, 23 and 25-29 are anticipated by Aharoni (U.S. Patent No. 5,480,944), that claims 24 and 30 are unpatentable over Aharoni in view of Fisch (U.S. Patent No. 5,760,163), that claims 1-5 and 7-9 are unpatetable over Aharoni in view of Meyer (U.S. Patent No. 4,255,560) and that claims 10-14 are unpatentable over Aharoni in

view of Meyer, and further in view of Fisch. For at least the reasons that follow, I disagree with the Examiner's conclusions.

(5) Based on my educational and professional experience in the field of chemistry, I am qualified to attest to the accuracy of the results of a comparative test, described below, which demonstrates that the thermoplastic polyamide according to the above-identified invention differs significantly from the polyamide of U.S. Patent No. 5,480,944 (hereinafter referred to as Aharoni). That is, the comparative test, described below, demonstrates that the polyamide of the above-identified invention differs significantly from the polyamide of Aharoni in terms of its molecular structure, composition, rheological characteristics and mechanical properties.

(6) **Description of Aharoni Polymers**

Aharoni relates to polyamide blends including one branched fractal polymer (FP) and linear polymers. In order to interpenetrate the linear polymer chains into three dimensional fractal polymer species, the fractal polymer should have the following characteristics:

(1) it should not be reactive with the end groups of the linear polymer in the polymeric matrix under preparation conditions;

(2) it should be "porous";

(3) the linear and fractal polymers must be compatible (i.e., having the same or very close solubility parameters).

6a). Synthesis and Characterization of Fractal Polymer

In the comparative test, I synthesized a fractal polymer representative of the

Aharoni polyamide by reacting one or more nucleus precursor monomers, $(Z_1)_a$-R_1-$(Z_2)_b$,

and one or more branching precursor monomers, $(Z_1)_c$-R_2-$(Z_2)_d$, in an aprotic solvent and

in the presence of effective amounts of phosphite compounds and a base. The variables a

and b are different and are integers, equal to 0 or $\geq$ 3, with the proviso that a or b is 0.

The variables c and d are different and are integers $\geq$ 1, with (c+d) $\geq$ 3. Z_1 is -OH or

-NH_2 and Z_2 is COOH or -N=C=O. More preferred function groups are -NH_2 for Z_1 and

-COOH for Z_2.

The structure and degree of branching are controlled by the relative values of a, b,

c and d. The greater the value of a, b, c and d, the greater the degree of branching and the

more rigid the fractal polymer obtained.

The porosity of the fractal polymer depends on the average distance between branch

points in the arms of the fractal polymers. For increased porosity, a difunctional extension

monomer can be used. The extension monomers are of the formulas: Z_1-R_3-Z_2, Z_1-R_3-Z_1,

or Z_2-R_3-Z_2.

When the nuclei monomer, branching monomer and extension monomer are R_1A_3

(trimesic acid), A_2R_2B (5-aminoisophtalic acid) and AR_3B (p-aminobenzoic acid)

respectively, the two-dimensional representation of the fractal polymer is shown in Figure

1.

Synthesis of fractal polymers is carried out in an aprotic solvent like

dimethylacetamide at temperatures in the range of 85-150°C. In addition, the reaction

requires the presence of an organic base, such as pyridine, and one or more phosphite
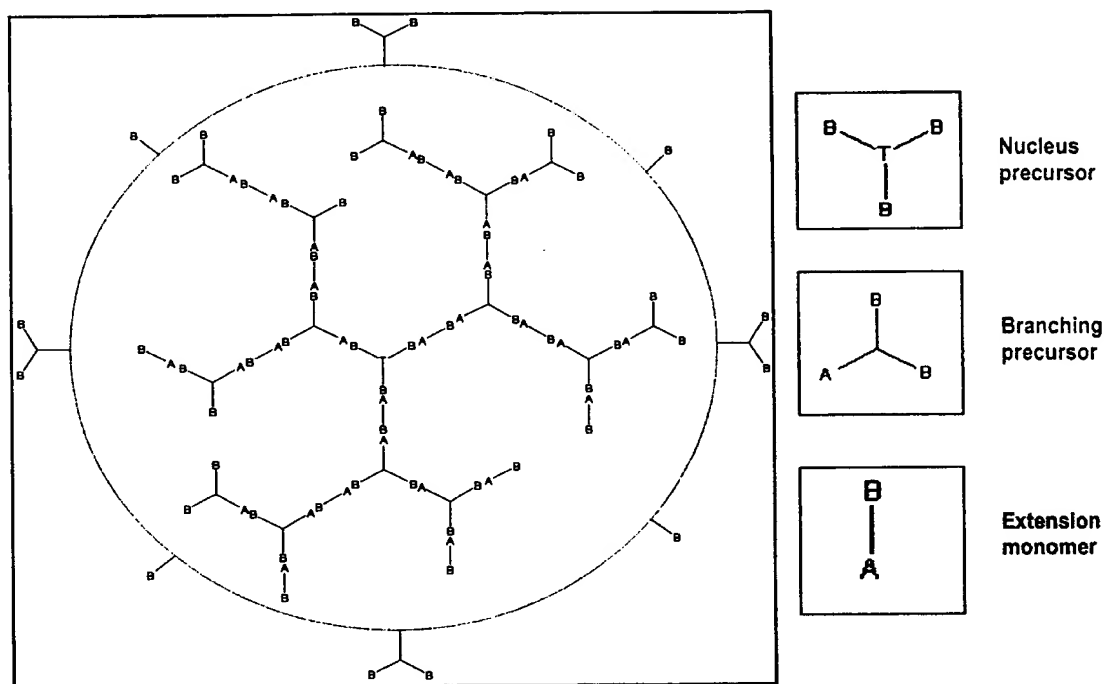
compounds as activating agents.

Figure 1. Topology of Aharoni Fractal Polymer

6b). Blends of Fractal Polymer with Linear Polyamide

The fractal polymers described in Aharoni are rigid and cannot be used as

thermoplastic polymers by themselves. However, the porosity of the fractal polymer

allows linear polymer chains to pass through and interpenetrate with the fractal polymer.

The claimed amount of linear matrix polymer is between 50% and 99% by weight.

Blends can be obtained by various methods including melt extrusion, batch melting, solution/precipitation, etc. The characteristics of the Aharoni blend include increased Young's modulus, yield strength and glass transition temperatures (Tg). Decreased solution and melt viscosities are also disclosed.

7.   Description and Characteristics of the Polyamide of the Present Application

The above-identified patent application discloses a thermoplastic polyamide with a high melt viscosity. The polyamide has a structure of the random-tree type obtained by polymerization of at least two monomers: a branching monomer $(Z_1)_a$-R_1-$(Z_2)_b$ and a difunctional monomer Z_1-R_2-Z_2, where Z_1 and Z_2 are -NH_2 and -$COOH$ respectively and a and b are integers. Optionally, the use of a monofunctional monomer as a chain regulator is defined in the claims.

It should be noted that the claimed composition is neither disclosed nor suggested by Aharoni. In particular, the nucleus precursor monomer present in the composition of Aharoni is not claimed in the present application.

The degree of branching (DB) in the claimed polyamide depends on the values of a and b and the mole ratio between the two monomers. In general, DB increases when the values of a and b and the mole ratio of $(Z_1)_a$-R_1-$(Z_2)_b$/Z_1-R_2-Z_2 are increased.

In the case of $(Z_1)_z$-R_1-$(Z_2)_b$ = A_2-R_1-B and Z_1-R_2=A-R_2-B, the structure of this tree-type copolymer is shown in Figure 2.
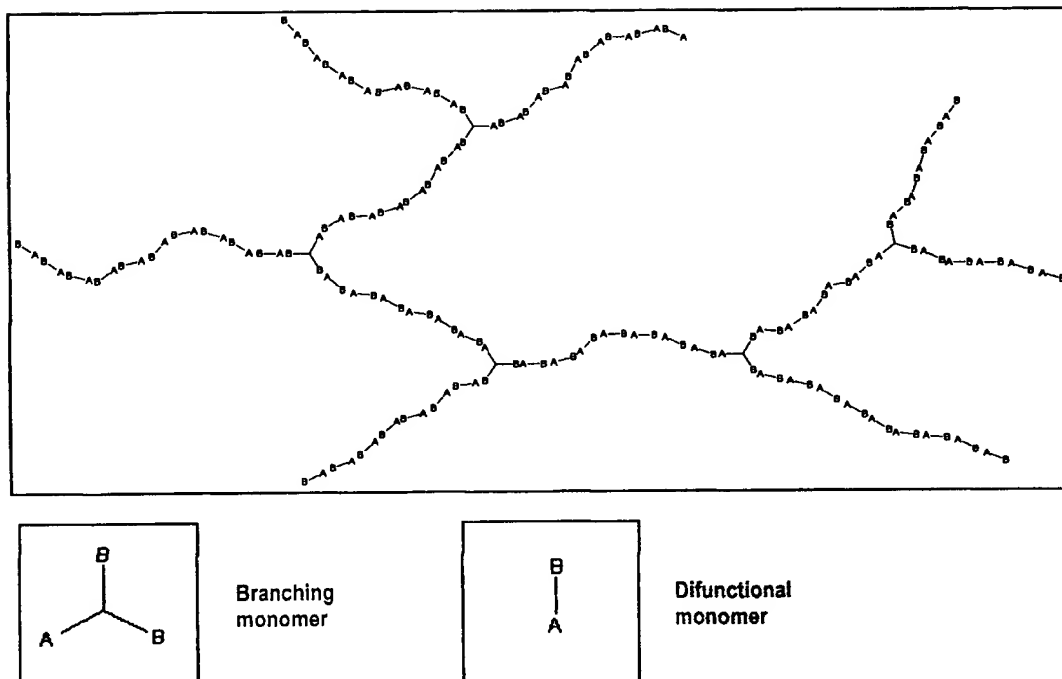
Figure 2. Topology of the claimed polyamide.

The synthesis of the polyamide is carried out by adding a predetermined amount of

branching monomer into the reaction mass of ε- caprolactame in a conventional process for

preparing Nylon6.

COMPARATIVE EXPERIMENTAL ANALYSIS OF PRODUCTS

8)   Preparation of Fractal Polymer According to Aharoni

According to Example I of Aharoni (see Aharoni, column 14, line 55), 350 grams

of so-called AB-type fractal polyamide were synthesized and coded A2105-78B. By

referring to Figure 1, the prepared fractal polymer corresponds to a 4-5-th generation of a Tomalia dendrimer.

9) Preparation of AB-Fractal and Nylon6 Blends, According to Aharoni

Blends were prepared using two different methods:

a) *Dissolution and Precipitation Method (see Aharoni at column 18, line 10)*

Three different blends were prepared by dissolving fractal polymer and linear Nylon 6 by precipitation in cold methanol. Blends containing 0.3% (SB 0.3%), 2.0% (SB 2.0%) and 7.0 % (w/w) of 5-aminisophtalic acid (AIA) (SB 7.0%) were prepared. The sample containing 7.0 % of AIA corresponds to a 12.5% (w/w) of fractal polymer in linear polyamide. In Aharoni, this sample exhibited the best properties. The composition containing 0.3% AIA was chosen in order to compare it directly to a reference composition of the above-identified patent application including the same amount of AIA in percentage.

b) *Compounding by single screw extrusion method (Goeffert Type/Kom 015/6768)*

Two samples (0.3% and 7.0% AIA) were prepared in the following conditions:

b1) 0.3% of AIA. Temperature profile: 261-266-267-272-277 °C; screw rate = 75 rpm; moment = 130 (FP 0.3%).

b2) 7.0 % of AIA; Temperature profile: 261-266-266-273-275; screw rate = 75 rpm; moment = 155 (FP 7.0 %).

**10)   Preparation of a tree-branched Nylon 6 According
        to the Present Application**

Two samples (129199 and 7303099) of tree-branched Nylon 6 were prepared in accordance with the present application having the following composition:

- CPL (Caprolactam) = 99.7 %

- AIA (5-amino-isophtalic acid) = 0.3%

Both samples were batch polymerized in mass in the classical conditions of Nylon 6 synthesis as described in the present application: CPL+AIA were added with 5% water and heated 12 hours at 270°C under N_2.

11)   Molecular Characterization of Polymers

Table 1 below presents the molecular masses and molecular mass distribution of the linear Nylon 6 used in the blend's preparation and of two tree-branched Nylon 6 samples provided by RHODIA (7303099 and 7129199). Size Exclusion Chromatography (SEC) analyses were performed, after N-trifluoroacetylation, in dry CH_2Cl_2 as eluent.

According to data disclosed in Aharoni and in agreement with its rigid structure, the fractal polymer is insoluble in these conditions and cannot be analyzed by SEC.

Table 1: SEC analysis of N-trifluoroacetylated samples.

Sample	Mn	Mw	Mz	D	Dz
Linear	17280	34455	52128	1.994	1.513
7303099	23769	48601	77249	2.045	1.589
7129199	24118	49604	80074	2.057	1.614

(12)   Rheological Properties of Materials

Figures 3 and 4 represent the rheological curves of Aharoni-type blends obtained by

dissolution/precipitation (solution blends SB) performed using a rotoviscosimeter Physica

MCR 300, at 230° and 250°C, respectively, and compared with

a pure linear polyamide and with a "RHODIA type" tree-branched Nylon 6 (sample

7303099).

Figure 5 represents rheological curves of blends of the same composition obtained

by extrusion performed at 250°C by a capillary viscosimeter Goeffert WinRHEO V3.22.

A comparison with a pure linear Nylon 6 and a "RHODIA-type" tree-branched Nylon 6

(sample 7303099) is again present.

The effect of different macromolecular architecture is clearly seen in all the figures.

The presence of fractal polymer decreases the viscosity of the blend as disclosed in

Aharoni while the melt viscosity of the tree-branched Nylon-6 is strongly increased, in

agreement with RHODIA's claims. The strong effect of the molecular architecture on the

melt viscosity can be evaluated by comparing curves of the tree-branched polyamide and of the blend with the same AIA content (0.3%).

In addition, the slope shape observed at 230°C in the 7.0 % solution blend and, more clearly, at 250°C in 2% and 7.0% blends suggests that the fractal polymer is not completely soluble in the linear polymer.
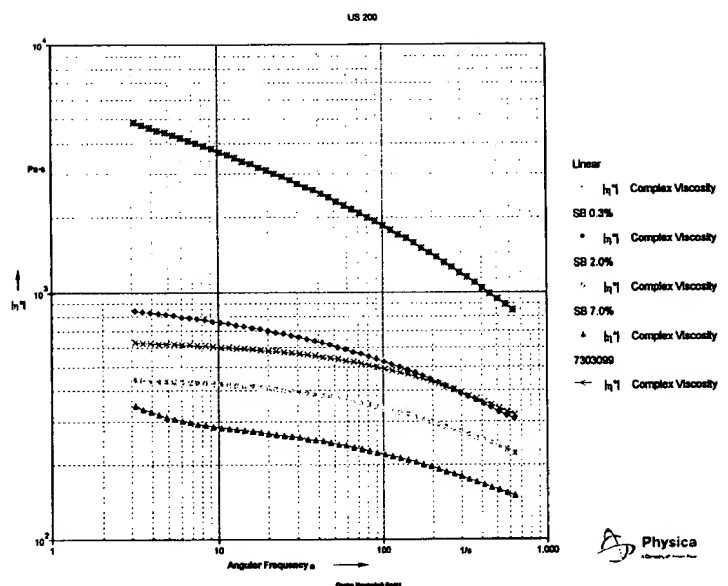
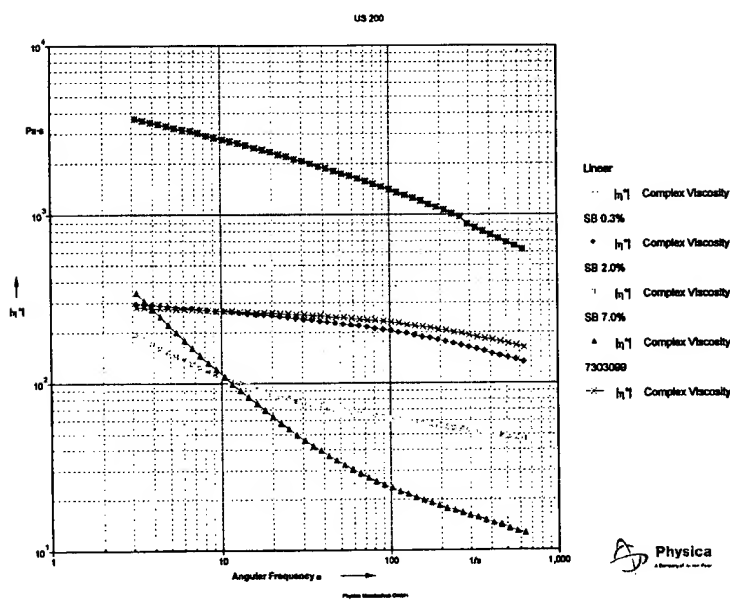Figure 3. Rheological curves of solution blends at 230 °C.

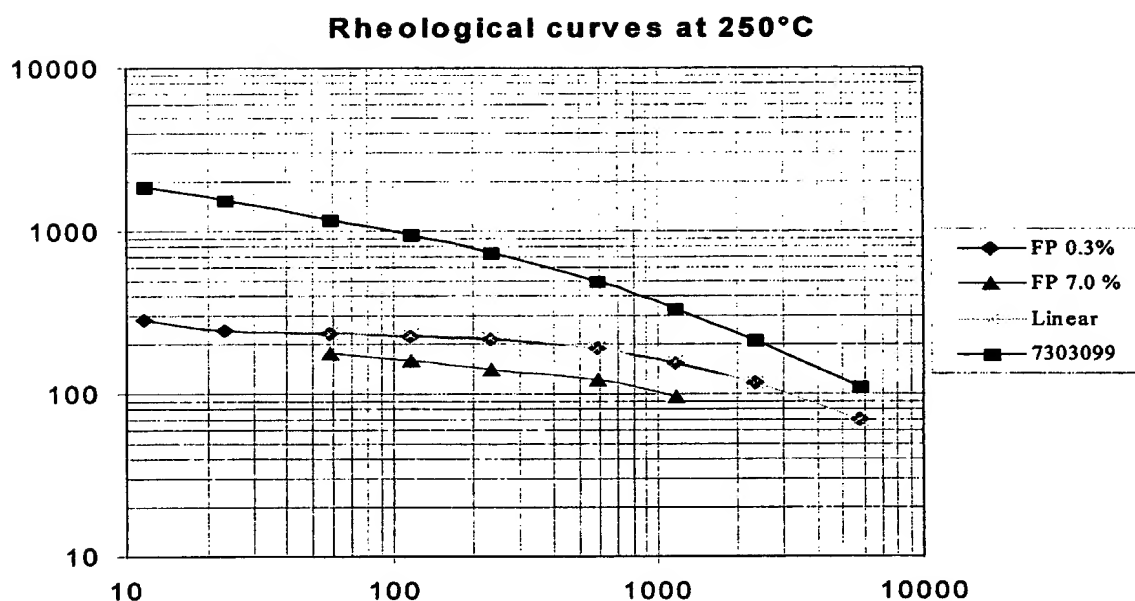Figure 4. Rheological curves of solution blends at 250 °C.

Rheological curves at 250°C

Figure 5. Rheological curves of melt blends at 250°C.

(13) Morphology of the Blends

Figure 6 compares the optical analyses of the Aharoni composition melt blend

fractal polymer 7.0% (7.05% of AIA, equivalent to 12.5% of fractal polymer in the blend)

and of a tree-branched "RHODIA type" polymer. The fractal component is visible as a

separated phase in both UV-filtered and polarized light. In stark contrast, the "RHODIA

type" polymer shows no sign of phase separation and has a homogeneous structure. This

conclusion is confirmed by SEM analysis of fracture surface depicted in Figures 7 and 8.

A loss in mechanical properties of the fractal blends should be linked to this poor
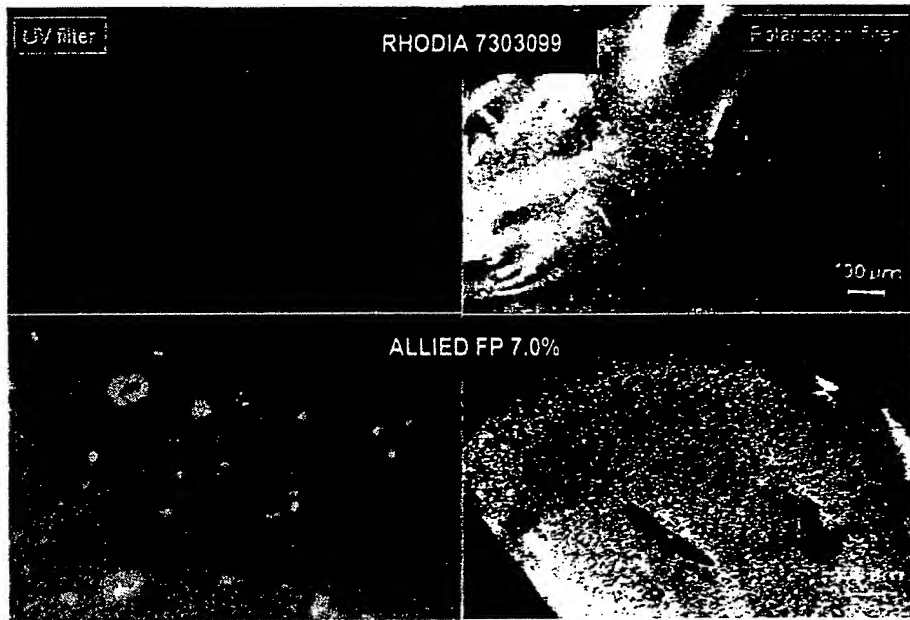
compatibility.

Figure 6. Pictures of a tree-branched RHODIA Nylon 6 and of an Aharoni blend.
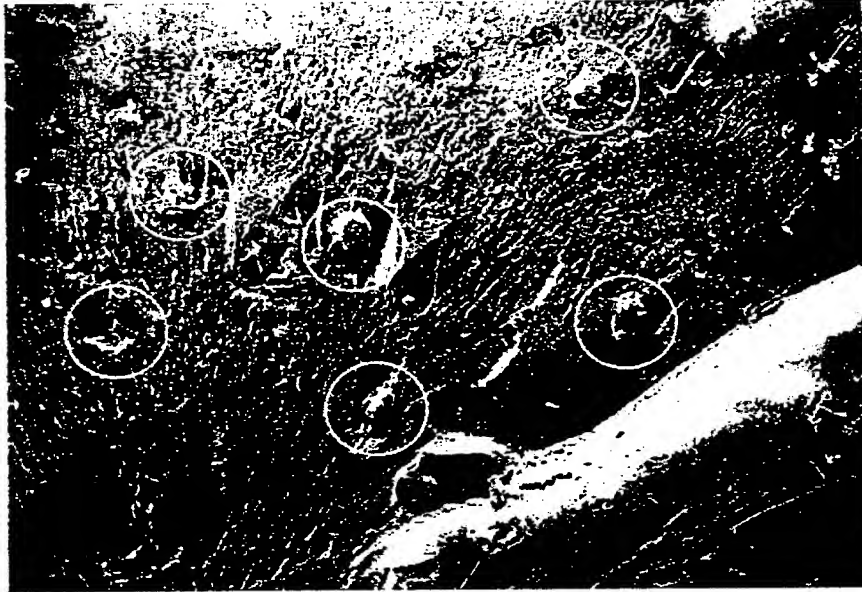
Figure 7. SEM pictures of the Aharoni polyamide blend FP 7.0%.

Figure 8. SEM picture of a tree-branched RHODIA Nylon 6.

(14)   Mechanical properties

Table 2 compares the mechanical properties of the Aharoni-type blends and two lots

of tree-branched Nylon 6 provided by RHODIA, vs linear nylon 6.

It is evident that the addition of fractal polymer in Nylon 6 produces a collapse of

mechanical properties. To the contrary, the tree-branched RHODIA polymer strongly

improves mechanical properties when compared with those of Nylon 6.

Table 2. Mechanical properties of linear polyamide, tree-polyamide and of

fractal/polyamide blend.

Sample	Linear	FP 0.3%	FP 7.0%	7129199	7303099
M.I. 325 M.I. 1000	7,4	9,2	5,3-13,5 19,4	 4,1	 5,5
NH$_2$ (meq\Kg COOH (meq\Kg)	52 52			37 53	29,7 56,1
IZOD notched(Kj/m^2)	**5,2**	**3,1**	**2,6**	**6,6**	**6,9**
Tensile elongation %	**90**	**2**	**1,1**	**140**	**190**
Tensile Modulus (N/mm2)	2850	2610	3060	2730	2980

CONCLUSIONS

The above comparative tests lead to the following conclusions:

a)   the molecular structure and composition of the Aharoni fractal polymer and its

blends with linear Nylon 6 are substantially different from the tree-branched RHODIA

polymer claimed in the above-identified patent application;

b)   The rheological characteristics of the Aharoni polymer and its blends are also substantially different from the claimed polymer.   That is, the blends of Aharoni show a decreased melt viscosity (vs linear Nylon 6 viscosity) with increased fractal polymer amount, in agreement with what is disclosed in Aharoni. In stark contrast, the claimed polymers show an increased melt viscosity compared to linear Nylon 6; and

c)   The Aharoni-type blends show biphasic structure, while the polymers of the above-identified patent application are monophasic and homogeneous in structure. This difference may also explain the substantial differences in the rheological and mechanical characteristics of the claimed polyamide as compared with the polyamide of Aharoni.

Therefore, in accordance with the knowledge obtained by the above comparative tests, I conclude:

1)   the claims of the above-identified patent application and Aharoni are directed to two different topologies of polyamide macromolecules, which differ, at least in part, due to the different monomer combination and synthetic processes used;

2)   because of these significantly different topologies, the claimed and observed properties of the claimed polyamide and the polyamide of Aharoni also differ significantly; and

3)   the claimed tree-branched polyamide therefore is neither disclosed nor suggested by the fractal blend disclosed in Aharoni.

I HEREBY DECLARE that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and

further that these statements were made with the knowledge that willful, false statements

and the like so made are punishable by fine or imprisonment, or both, under Section 1001

of Title 18 of the United States Code and that such willful, false statements may jeopardize

the validity of the application or any patent issued thereon.

Date: _9/07/03_   By: _____

Dr. Giuseppe Di Silvestro

<u>**APPENDIX I**</u>

Curriculum Vitae and Scientific Activity

of Prof. Giuseppe Di Silvestro